

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization  
International Bureau



(43) International Publication Date  
13 March 2003 (13.03.2003)

PCT

(10) International Publication Number  
WO 03/020423 A1

(51) International Patent Classification<sup>7</sup>: B01J 29/08, 37/00, C10G 11/05

(21) International Application Number: PCT/US02/25023

(22) International Filing Date: 7 August 2002 (07.08.2002)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:  
09/942,971 31 August 2001 (31.08.2001) US

(71) Applicant: ENGELHARD CORPORATION [US/US];  
101 Wood Avenue, P.O. Box 101, Iselin, NJ 08830-0770 (US).

(72) Inventors: GIBSON, Clark, W.; 1507 Dogwood Drive, Bainbridge, GA 31717 (US). WILLIS, Mitchell, J.; 1802 Woodbridge Drive, Bainbridge, GA 31717 (US). GANTT, George, E.; 200 Kenan Drive NW, Milledgeville, GA 31061 (US). BARNES, Robert, E.; 200 Kenan Drive NW, Milledgeville, GA 31061 (US). BARNES, Robert, E.; 5 Hoover Creek Road, Savannah, GA 31419 (US). STOCKWELL, David, M.; 202 Ashland Road, Middlesex, NJ 08846 (US).

(74) Agents: HAMPILOS, Gus, T. et al.; Engelhard Corporation, 101 Wood Avenue, P.O. Box 770, Iselin, NJ 08830-0770 (US).

(81) Designated States (*national*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, UZ, VN, YU, ZA, ZM, ZW.

(84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

**Declaration under Rule 4.17:**

— *as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii)) for all designations*

**Published:**

— *with international search report*

*For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.*

(54) Title: FCC CATALYST MANUFACTURING PROCESS

(57) Abstract: An in situ process for making improved zeolitic fluid cracking catalysts by spray drying a mixture of (i) hydrous kaolin and/or metakaolin, and (ii) calcined aluminum source, said calcined aluminum source being derived from a pulverized, ultra-fine kaolin, calcining the resulting microspheres to convert hydrous kaolin to metakaolin, and reacting microspheres composed of a mixture of metakaolin and calcined aluminum source with an alkaline sodium silicate solution. The weight percent of metakaolin in the calcined microspheres is greater than the calcined aluminum source content.

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## FCC CATALYST MANUFACTURING PROCESS

BACKGROUND OF THE INVENTION

5        This invention relates to improvements in zeolitic fluid cracking catalysts (FCC) produced by an in situ reaction between an alkaline sodium silicate solution and microspheres composed of a mixture of two different forms of calcined kaolin clay, so-called "metakaolin" and "spinel".  
10      The former is sometimes referred to as "reactive" calcined kaolin and the latter as "kaolin calcined through the characteristic exotherm".

      For many years a significant proportion of commercial FCC catalysts used throughout the world have been made by in situ synthesis from precursor microspheres containing kaolin  
15      that has been calcined at different severities prior to formation into microspheres by spray drying. Generally, these fluid cracking catalysts are microspheres composed of zeolite Y and matrix material, typically silica alumina.  
20      U.S. Patent No. 4,493,902 to Brown et al., the teachings of which are incorporated herein by cross-reference, discloses fluid cracking catalysts comprising attrition-resistant, high zeolite content, catalytically active microspheres containing more than about 40%, preferably 50-70% by weight  
25      Y faujasite and methods for making such catalysts by crystallizing more than about 40% sodium Y zeolite in porous microspheres composed of a mixture of two different forms of chemically reactive calcined clay, namely, metakaolin (kaolin calcined to undergo a strong endothermic reaction  
30      associated with dehydroxylation) and kaolin clay calcined under conditions more severe than those used to convert kaolin to metakaolin, i.e., kaolin clay calcined to undergo the characteristic kaolin exothermic reaction, sometimes

referred to as the spinel form of calcined kaolin. In preferred embodiments, the microspheres containing the two forms of calcined kaolin clay are immersed in an alkaline sodium silicate solution, which is heated, preferably until  
5 the maximum obtainable amount of Y faujasite is crystallized in the microspheres.

In the practice of the '902 technology, the porous microspheres in which the zeolite is crystallized are preferably prepared by forming an aqueous slurry of powdered  
10 raw (hydrated) kaolin clay ( $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$ ) and powdered calcined kaolin clay that has undergone the exotherm together with a minor amount of sodium silicate which acts as fluidizing agent for the slurry that is charged to a spray dryer to form microspheres and then functions to  
15 provide physical integrity to the components of the spray dried microspheres. The spray dried microspheres containing a mixture of hydrated kaolin clay and kaolin calcined to undergo the exotherm are then calcined under controlled conditions, less severe than those required to cause kaolin  
20 to undergo the exotherm, in order to dehydrate the hydrated kaolin clay portion of the microspheres and to effect its conversion into metakaolin, this resulting in microspheres containing the desired mixture of metakaolin, kaolin calcined to undergo the exotherm and sodium silicate binder.  
25 In illustrative examples of the '902 patent, about equal weights of hydrated kaolin and spinel are present in the spray dryer feed and the resulting calcined microspheres contain somewhat more kaolin that has undergone the exotherm than metakaolin. The '902 patent teaches that the calcined  
30 microspheres comprise about 30-60% by weight metakaolin and about 40-70% by weight kaolin characterized through its characteristic exotherm. It is to be noted that no

metakaolin is present in the spray dryer feed used in the preferred manufacturing process described in the '902 patent. A less preferred method described in the patent, involves spray drying a slurry containing a mixture of  
5 kaolin clay previously calcined to metakaolin and kaolin calcined to undergo the exotherm but without including any hydrated kaolin in the slurry, thus providing microspheres containing both metakaolin and kaolin calcined to undergo the exotherm directly, without calcining to convert hydrated  
10 kaolin to metakaolin. However, the patent teaches that less attrition zeolitized microspheres are produced by this approach.

In carrying out the invention described in the '902 patent, the microspheres composed of kaolin calcined to  
15 undergo the exotherm and metakaolin are reacted with a caustic enriched sodium silicate solution in the presence of a crystallization initiator (seeds) to convert silica and alumina in the microspheres into synthetic sodium faujasite (zeolite Y). The microspheres are separated from the sodium  
20 silicate mother liquor, ion-exchanged with rare earth, ammonium ions or both to form rare earth or various known stabilized forms of catalysts. The technology of the '902 patent provides means for achieving a desirable and unique combination of high zeolite content associated with high  
25 activity, good selectivity and thermal stability, as well as attrition-resistance.

The zeolite content of the crystallized microspheres is determined by X-ray diffraction from the zeolite, which is best performed on the sodium form crystallized microspheres.  
30 Conventional chemical analytical techniques are not deemed to be applicable to the determination of the zeolite content of materials in which the zeolite is crystallized in situ in

a silica-alumina matrix, which cannot be readily physically or chemically isolated. In practice, it has been found that the apparent amount of zeolite crystallized from any given formulation using the '902 technology can vary, depending on the history of raw material, processing conditions and proportions and concentrations of reagents. The zeolite content (sodium form) of crystallized microspheres range from 40% to 72% in illustrative examples of the '902 patent. Commercial production and laboratory preparations typically result in the crystallization of a maximum of about 55-60% zeolite (sodium form). Since at least a substantial proportion of the zeolite grows in macropores of the precursor porous microspheres, it might be expected that simply increasing macroporosity of the precursor microspheres would result in the generation of higher levels of zeolite because more space would be available in which to grow zeolite crystals.

Surprisingly, merely providing more room for crystal growth by increasing macroporosity will not achieve this result.

The aforementioned technology has met widespread commercial success. Because of the availability of high zeolite content microspheres which are also attrition-resistant, custom designed catalysts are now available to oil refineries with specific performance goals, such as improved activity and/or selectivity without incurring costly mechanical redesigns. A significant portion of the FCC catalysts presently supplied to domestic and foreign oil refiners is based on this technology.

U.S. 5,023,220 to Dight et al. discloses an economically attractive method for increasing the zeolite content of high zeolite content kaolin derived microspheres

obtained by reacting precursor microspheres composed of a mixture of metakaolin and kaolin calcined to undergo the exotherm with a sodium silicate solution to crystallize zeolite Y in situ in macropores of the precursor microspheres. The increase in zeolite content is associated with a desirable increase in catalytic activity and seems to improve selectivity. Improvements in activity and selectivity, specifically a reduction in coke and/or gas make are desirable. Reductions in coke or gas make or both serves the needs of refiners whose FCC units are limited by regenerator temperature, air blower and/or gas compressors.

The zeolite microspheres of the invention disclosed in Dight et al. are produced by novel processing, which is a modification of technology described in the '902 patent, and involves increasing the proportion of calcined kaolin in the form of metakaolin to kaolin calcined to undergo the exotherm in the porous precursor microspheres in which zeolite Y is crystallized while also increasing the macroporosity of the precursor microspheres. The increase in macroporosity is preferably achieved by increasing the ratio of calcined kaolin to hydrated kaolin in the slurry that is spray dried to produce the porous precursor microspheres. In this manner, both spatial and nutritional limitations to the growth of zeolite Y are alleviated and therefore ultrahigh levels of zeolite (e.g, ca. 75% able to be crystallized). Known post-zeolite synthesis processing (ion-exchange, etc.) may be practiced to produce octane versions of these catalysts.

U.S. Patent No. 5,395,809 to Madon et al. found that the proportions of hydrous kaolin and fully calcined kaolin contained in the microsphere prior to in situ zeolite growth will significantly affect the properties and performance of

the resulting catalyst. Furthermore, the resulting properties and performance attributes such as coke yield, bottoms upgrading, metals resistance, zeolite stability, activity and ease of sodium removal do not vary linearly with the proportions of hydrous kaolin and fully calcined kaolin. As a result there is a certain range or window where all or most of the desirable properties and performance attributes are at or near optimal. The boundaries of this window are defined by the weight ratio or hydrous to fully calcined kaolin and are approximately 90:10 to 60:40.

The preferred method for making such catalysts in accordance with U.S. 5,395,809 involves initially preparing microspheres composed of combinations of hydrous kaolin and spinel such that the initial hydrous kaolin content, expressed as weight percent, is greater than the spinel content and the microspheres, at this point of the process, are essentially free from metakaolin. The microspheres also contain a binder, usually equal to or greater than 5 wt. % of the spray-dried particles, which is provided by the addition of a sodium silicate solution. The microspheres are calcined at a predetermined temperature to convert the hydrous kaolin to metakaolin without altering the spinel level. In situ Y zeolite FCC catalyst are then made from these microspheres by subsequent crystallization in a seeded sodium silicate solution and ion exchanged to reduce sodium level.

Catalysts of U.S. 5,395,809 have improved stability and are very active and have improved sodium removal with respect to the prior art at that time. The ease of sodium removal and high activity with concurrent low dry gas and coke yields make these modified microsphere catalysts

excellent candidates for high octane catalysts, high isobutylene catalysts and improved bottoms upgrading catalysts.

Still, the art is constantly seeking ways to improve zeolite FCC catalysts to improve either one or more of attrition resistance, activity, selectivity, and ease of sodium removal. Such improvement forms the basis of this invention.

10 SUMMARY OF THE INVENTION

In accordance with this invention, novel zeolite microspheres are produced by crystallizing calcined, spray-dried, microspheres formed from an aqueous slurry containing (i) hydrated kaolin clay, metakaolin or mixtures thereof, (ii) a specifically defined calcined aluminum source and (iii) a binder. The calcined aluminum source (ii) is a kaolin clay which has been calcined through its characteristic exotherm and which itself is derived from a pulverized, ultrafine kaolin clay, or the calcined aluminum source is a calcined aluminum-containing material which has an Incipient Slurry Point of less than 57% solids. The Incipient Slurry Point is defined below and concerns the minimum amount of water needed to form a flowable mass of the calcined aluminum-containing material. The pulverized ultrafine kaolin clay has a particulate size such that 90% weight of the hydrous kaolin particles are less than 2.0 microns.

The calcined aluminum source (ii) contained in the slurry forms the non-zeolite matrix of the catalyst.

30 Utilizing the specified materials for the calcined aluminum source (ii), non-macroporous, in-situ zeolite microspheres are produced in which the matrix is highly dispersed

zeolitic component (matrix) of the catalysts of the present invention is derived from a specifically defined calcined aluminum source (ii). One such source is a hydrous kaolin that is in the form of an ultrafine powder in which at least  
5 90 wt. % of the particles are less than 2.0 microns, preferably at least 90 wt. % less than 1 micron, and which has been pulverized and calcined through its characteristic exotherm.

Typical prior art zeolite microspheres have a matrix  
10 formed from a hydrous kaolin having a larger size than used in this invention and which is calcined at least substantially through its characteristic exotherm.

Satintone® No. 1, calcined kaolin (a commercially available kaolin that has been calcined through its characteristic  
15 exotherm without any substantial formation of mullite) is a material which has been used on a commercial basis.

Satintone® No. 1 is derived from a hydrous kaolin in which 70% of the particles are less than 2 microns. Other sources to form the matrix have been used including finely divided  
20 hydrous kaolin (e.g., ASP® 600, a commercially available hydrous kaolin described in Engelhard Technical Bulletin No. TI-1004, entitled "Aluminum Silicate Pigments" (EC-1167)) calcined at least substantially through its characteristic exotherm. Booklet clay has found the most widespread  
25 commercial use and has met tremendous success worldwide. Before the present invention, these larger clay particles represented the state of the art and had no perceived deficits.

What is meant by "ultrafine" is that at least 90 wt. %  
30 of the particles of the pulverized, hydrous kaolin must be less than 2 microns in diameter, preferably less than 1

throughout the catalyst instead of being in the form of islands of matrix which occurs when coarser booklet clay particles are used. The zeolite microspheres of this invention have less than 0.07 cc/gm mercury intrusion of pores in the 600-20,000 angstrom range. The zeolite microspheres of this invention have a high surface area and as well, sodium-ammonium equilibrium isotherms are also improved, providing for efficient ion exchange. These advantages are obtained with no loss of selectivity or attrition resistance. These properties are valued in the market served by the zeolite FCC technology.

#### DETAILED DESCRIPTION OF THE INVENTION

Catalysts of the invention are made from precursor porous microspheres composed of calcined kaolin of which a major weight portion is metakaolin and a minor weight proportion is a calcined aluminum source and a sodium silicate binder. The weight ratio of metakaolin to calcined aluminum source in the precursor microspheres is greater than 1:1, preferably greater than 1.25:1. The level of binder as SiO<sub>2</sub> in the microspheres ranges from about 2 to 25 wt. %, preferably 5-17 wt. % based on the weight of the microspheres. The precursor microspheres are reacted with zeolite seeds and an alkaline sodium silicate solution. The microspheres are crystallized to a desired zeolite content (typically at least 50% and preferably, at least 70%), filtered, washed, ammonium exchanged, exchanged with rare-earth cations if required, calcined, exchanged a second time with ammonium ions, and calcined a second time if required.

The catalyst microspheres of this invention are produced by the general process as disclosed in commonly assigned U.S. Patent No. 5,395,809. Importantly, the non-

micron determined by Sedigraph™ (or sedimentation). It has been found that, in particular, use of hydrous kaolin with this particle size distribution upon pulverization and calcination through the characteristic exotherm results in a  
5 microsphere having a greater quantity of macroporosity. The loose packing of the calcined ultrafine kaolin can be likened to a "house of cards" in which the individual particulates are aligned randomly with respect to adjacent particles in a non-parallel manner. Moreover, the calcined,  
10 pulverized kaolin exists as porous aggregates of the "house of cards" morphology, providing not only a porous aggregate but additional porous areas between aggregates. Pulverization of the ultrafine hydrous kaolin is required before calcination through the exotherm in order to provide  
15 the random stacking of the individual kaolin platelets.

The need to increase the pore volume of the microspheres so as to increase the ultimate zeolite content of the catalysts to levels consistently greater than 50% is disclosed in the above-mentioned U.S. patent 5,023,220 to  
20 Dight et al. The pore volume of the microspheres decreases as the zeolite crystals grow, hence the need for sufficient initial pore volume to yield large zeolite content. Dight et al. increases pore volume by adding metakaolin powder to the microspheres. Metakaolin is more porous than hydrous  
25 kaolin. Unfortunately, substantially more water must be used in slurries made from mixtures of metakaolin and kaolin clay that has been calcined through its characteristic exotherm than in slurries made from mixtures of hydrous kaolin and kaolin clay that has been calcined through its  
30 characteristic exotherm in order to obtain a slurry that is suitable for spray drying. The reason for this is that

slurries made from mixtures of metakaolin and kaolin clay that has been calcined through its characteristic exotherm are, at a given water content, more viscous than slurries made from mixtures of hydrous kaolin and kaolin that has  
5 been calcined through its characteristic exotherm. Of course, substantially increasing the amount of water in the slurry that is spray dried increases the amount of water that must be evaporated in the spray drying step and adds to the expense of the spray drying step. Madon et al.  
10 discloses in U.S. 5,395,809 the use of coarser hydrous kaolin and high silicate binder levels to improve microsphere porosity. One disadvantage of such process is that the high soda content due to the binder leads to trapping of soda in the microsphere and causes exchange  
15 inefficiencies. In the present invention, effective pore volume in the microsphere is obtained by use of the calcined, pulverized ultrafine kaolin which also appears to improve sodium removal.

Kaolin clays or pigments are naturally-occurring  
20 hydrated aluminum silicates of the approximate formula  $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot \text{XH}_2\text{O}$ , wherein X is usually 2. Kaolinite, nacrite, dickite and halloysite are species of minerals in the kaolin group. It is well known that when hydrous kaolin is heated in air, that a first transition occurs at about  
25  $550^\circ \text{C}$ . associated with an endothermic dehydroxylation reaction. The resulting material is generally referred to as metakaolin. Metakaolin persists until the material is heated to about  $975^\circ \text{C}$ . and begins to undergo an exothermic reaction. This material is frequently described as kaolin,  
30 which has undergone the characteristic exothermic reaction. Some authorities refer to this material as a defect aluminum-silicon spinel or as a gamma alumina phase. See

Donald W. Breck, Zeolite Molecular Sieves, published by John Wiley and Sons, 1974, pp. 314-315. On further heating to about 1,050° C., high temperature phases including mullite begin to form. The extent of conversion to mullite is  
5 dependent on a time-temperature relationship and the presence of mineralizers, as is well-known in the art.

In the preferred embodiments of this invention, the pulverized, ultrafine hydrous kaolin used as the calcined aluminum source is calcined through its characteristic  
10 exotherm with or without the formation of mullite. An especially preferred calcined aluminum matrix source which is used in this invention to form the zeolite microspheres is Ansilex® 93. Ansilex® 93 is made from the fine size fraction of a hard kaolin crude, by spray drying,  
15 pulverizing and calcining to prepare low abrasion pigments as described in U.S. Patent No. 3,586,523, to Fanselow, et. al., the entire contents of which are herein incorporated by reference. The fine fraction of hard kaolin crude is spray dried, pulverized and then calcined beyond the  
20 characteristic exotherm. What is unusual about the use of the Ansilex® material is that it is derived from hard kaolin clay. Hard kaolin clays typically have a gray tinge or coloration and are further characterized by breaking into irregularly shaped fragments having rough surfaces. Such  
25 hard kaolin clays are also called "gray" clays. Hard kaolin clays also contain a significant iron content, typically from about 0.6 to 1 wt. % of Fe<sub>2</sub>O<sub>3</sub>. Hard kaolin clays are described in Grim's "Applied Clay Mineralogy", 1962, McGraw Hill Book Company, pp. 394-398 thereof, the  
30 disclosure of which is incorporated by reference herein. The use of these materials as the calcined aluminum source to form the matrix for in situ FCC microsphere catalysts has

not been known previous to commonly assigned, copending application, U.S. Serial No. 09/667,677 filed September 22, 2000. The present application is distinguished from 09/667,677 in that the present invention provides for a  
5 substantially non-macroporous catalyst, i.e. a total mercury pore volume of no greater than 0.15 cc/gm.

The use of hard kaolin clays in the incorporated routes to forming zeolite/matrix catalysts is well established. Hard kaolin clays have also occasionally been used as  
10 sources of metakaolin for in situ microspheres, but not with advantage. Without wishing to be bound by any theory, it would appear that previous use of the calcined hard kaolin in the in situ matrix art would be precluded by (a) their high iron content and a possibility that this could lead to  
15 coke and gas production, and (b) the dilatant nature of their slurries, leading to apparently senseless waste of process time and increased costs in making down high viscosity slurries which spray dry at low solids. We now believe these dilatancy problems and porosity benefits are  
20 intrinsically and fundamentally linked. As for the former point, reduced coke and gas was an especially sought-after object for in situ catalysts, since the prior art formulations made coke and gas commensurate with their extraordinarily high level of amorphous matrix activity.  
25 This led to lower and lower levels of iron and spinel in subsequent inventions. There now appears to be no relationship between the iron and coke and gas selectivities after all.

The calcined aluminum source useful in this invention  
30 can be more generally characterized by the porosity thereof provided during the packing of the calcined material. A test has been developed to determine the pore volume of the

calcined aluminum source. The test characterizes the water pore volume of the calcined aluminum source by determining the minimum amount of water needed to make a slurry from a sample of the solids. In the test, a powder sample is mixed with water containing a dispersant such as, for example, Colloid 211, Viking Industries, Atlanta, GA, in a cup using a stirring rod or spatula. Just enough water is added to the dry sample to convert the dry powder to a single mass of dilatant mud, which only just begins to flow under its own weight. The incipient slurry point (ISP) is calculated from the weights of the sample and water used. This amount of water is larger than the water pore volume of the sample, but is clearly related to the water pore volume. Lower incipient slurry point percent solids values indicate higher water absorption capacities or higher pore volume in the sample. The incipient slurry point can be calculated as follows:  $ISP = [(grams\ of\ dry\ sample) / (grams\ of\ dry\ sample\ plus\ grams\ of\ water\ added)] \times 100$ . The units are dimensionless and are reported as percent solids.

The calcined aluminum sources used in this invention will have incipient slurry points of less than 57% solids, preferably 48 to 52% solids. An example of such material is Ansilex® 93 from Engelhard Corporation. Additionally, it has been found that delaminated kaolin, upon pulverization and calcination beyond the characteristic exotherm also has a high water pore volume with an ISP typically below 50% which would be very effective in forming the non-macroporous FCC catalyst microspheres of this invention. This compares with previously used calcined aluminum sources for matrix formation such as Satintone® No. 1 or spinel made from NoKarb booklet kaolin which yield over 58% in the incipient slurry point test.

Accordingly, not only is the pulverized, ultrafine hydrous kaolin useful as the aluminum source, but the aluminum source may also be obtained from delaminated kaolin, platelet alumina and precipitated alumina. Means  
5 for delaminating booklets or stacks of kaolin are well-known in the art. Preferred are those methods, which use a particulate grinding medium such as sand, or glass microballoons as is well-known. Subsequent to delamination, the platelets are pulverized to derive the random packing or  
10 "house of cards" morphology and then calcined.

The reactive component (i) of the slurry to form the microspheres can be formed of hydrated kaolin or calcined hydrous kaolin (metakaolin) or mixtures thereof. The hydrous kaolin of the feed slurry can suitably be either one  
15 or a mixture of ASP<sup>®</sup> 600 or ASP<sup>®</sup> 400 kaolin, derived from coarse white kaolin crudes. Finer particle size hydrous kaolins can also be used, including those derived from gray clay deposits, such as LHT pigment. Purified water-processed kaolin clays from Middle Georgia have been used  
20 with success. Calcined products of these hydrous kaolins can be used as the metakaolin component of the feed slurry. Silicate for the binder is preferably provided by sodium silicates with SiO<sub>2</sub> to Na<sub>2</sub>O ratios of from 1.5 to 3.5 and especially preferred ratios of from 2.88 to 3.22.

25 In a preferred embodiment of the invention an aqueous slurry of finely divided hydrated kaolin clay and/or metakaolin, and pulverized, ultrafine kaolin that has been calcined through its characteristic exotherm and sodium silicate binder is prepared. The aqueous slurry is then  
30 spray dried to obtain microspheres comprising a sodium silicate bonded mixture of hydrated kaolin and/or metakaolin and the pulverized, ultrafine kaolin that has been calcined

at least substantially through its characteristic exotherm.

The microspheres have average particle diameters that are typical of commercial fluid catalytic cracking catalysts, e.g., 65-85 microns. Suitable spray drying conditions are  
5 set forth in the '902 patent.

A quantity (e.g., 3 to 30% by weight of the kaolin) of zeolite initiator may also be added to the aqueous slurry before it is spray dried. As used herein, the term "zeolite initiator" shall include any material containing silica and  
10 alumina that either allows a zeolite crystallization process that would not occur in the absence of the initiator or shortens significantly the zeolite crystallization process that would occur in the absence of the initiator. Such materials are also known as "zeolite seeds". The zeolite  
15 initiator may or may not exhibit detectable crystallinity by x-ray diffraction.

Adding zeolite initiator to the aqueous slurry of kaolin before it is spray dried into microspheres is referred to herein as "internal seeding". Alternatively,  
20 zeolite initiator may be mixed with the kaolin microspheres after they are formed and before the commencement of the crystallization process, a technique which is referred to herein as "external seeding".

The zeolite initiator used in the present invention may  
25 be provided from a number of sources. For example, the zeolite initiator may comprise recycled fines produced during the crystallization process itself. Other zeolite initiators that may be used include fines produced during the crystallization process of another zeolite product or an  
30 amorphous zeolite initiator in a sodium silicate solution. As used herein, "amorphous zeolite initiator" shall mean a

zeolite initiator that exhibits no detectable crystallinity by x-ray diffraction.

The seeds may be prepared as disclosed by in 4,493,902. Especially preferred seeds are disclosed in 4,631,262.

5 After spray drying, the microspheres may be calcined directly, or alternatively acid-neutralized to further enhance ion exchange of the catalysts after crystallization.

The acid-neutralization process comprises co-feeding uncalcined, spray dried microspheres and mineral acid to a stirred slurry at controlled pH. The rates of addition of solids and acid are adjusted to maintain a pH of about 2 to 7, most preferably from about 2.5 to 4.5 with a target of about 3 pH. The sodium silicate binder is gelled to silica and a soluble sodium salt, which is subsequently filtered and washed free from the microspheres. The silica gel-bound microspheres are then calcined. In either case, calcination is done at a temperature and for a time (e.g., for two hours in a muffle furnace at a chamber temperature of about 1,350° F.) sufficient to convert any hydrated kaolin component of the microspheres to metakaolin, leaving the previously calcined kaolin components of the microspheres essentially unchanged. The resulting calcined porous microspheres comprise a mixture of metakaolin and kaolin clay calcined through its characteristic exotherm in which the two types of calcined kaolin are present in the same microspheres. Most preferably the calcined microspheres comprise metakaolin and kaolin that has been calcined through its characteristic exotherm or, alternatively any appropriate calcined aluminum source as previously described, in a weight ratio of metakaolin to calcined aluminum source of greater than 1:1, preferably greater than 1.25:1. Also

present is  $\text{Na}_2\text{O}$  and  $\text{SiO}_2$  derived from sodium silicate binder.

Y-faujasite is allowed to crystallize by mixing the calcined kaolin microspheres with the appropriate amounts of  
5 other constituents (including at least sodium silicate and water), as known in the art, and then heating the resulting slurry to a temperature and for a time (e.g., to  $200^\circ\text{--}215^\circ\text{F.}$  for 10-24 hours) sufficient to crystallize at least about 50% by weight, preferably at least about 70% by weight, Y-  
10 faujasite in the microspheres. Crystallization of zeolite Y is discussed in aforementioned U.S. Patent Nos. 5,023,220 and 4,493,902, the entire contents of which are herein incorporated by reference.

The calcined kaolin microspheres are mixed with one or  
15 more sources of sodium silicate and water to form a slurry. Sodium hydroxide may be included in the slurry to adjust the  $\text{Na}_2\text{O}$  content in the solution phase to an appropriate level as is known. Zeolite initiator is also added from a source separate from the kaolin if it had not previously been added  
20 (e.g. by internal seeding).

The crystallization recipes employed are based on a set of assumptions and certain raw materials. The seeds are described by 4,631,262 and have been used only externally, recently. The  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ , and  $\text{Na}_2\text{O}$  components of  
25 metakaolin, seeds, sodium silicate solution, calcined sodium silicate binder, and silica gel are assumed to be 100% reactive. The alumina and silica in kaolin calcined through the exotherm to the spinel form are assumed to be 1% and 90% reactive respectively. Although these two values are in  
30 use, they are not believed to be accurate. The alumina and silica in kaolin calcined through the exotherm to mullite are assumed to be 0% and 67% reactive, respectively. These.

two values are believed to be accurate, representing the inertness of 3:2 mullite in crystallization and the full solubility of the free silica phase.

Using these assumptions, the following weight ratios  
5 for reactive components are used in the overall crystallization recipes. Inert components do not enter into the ratios, except in the case of the seeds dose, which is defined as the ratio of the grams of seeds  $\text{Al}_2\text{O}_3$  to total grams of microspheres.

10

Weight Ratios	$\text{SiO}_2/\text{Na}_2\text{O}$	$\text{SiO}_2/\text{Al}_2\text{O}_3$	$\text{H}_2\text{O}/\text{Na}_2\text{O}$	Seeds $\text{Al}_2\text{O}_3/\text{MS}$
Broadly	2.50-3.1	4.5-15	5-15	.01-0.0001
Preferred	2.55-2.95	5.5-8	5.5-8	0.006-0.001
Typical (spinel)	2.75	7.0	7.0	0.004
(Acid-Neutr)	2.9			

The sodium silicate and sodium hydroxide reactants may be added to the crystallization reactor from a variety of sources. For example, the reactants may be provided as an  
15 aqueous mixture of N<sup>®</sup> Brand sodium silicate and sodium hydroxide. As another example, at least part of the sodium silicate may be provided by the mother liquor produced during the crystallization of another zeolite-containing product.

20 After the crystallization process is terminated, the microspheres containing Y-faujasite are separated from at least a substantial portion of their mother liquor, e.g., by filtration. It may be desirable to wash the microspheres by contacting them with water either during or after the  
25 filtration step. The purpose of the washing step is to remove mother liquor that would otherwise be left entrained within the microspheres.

"Silica Retention" may be practiced. The teachings of U.S. Patent No. 4,493,902 at column 12, lines 3-31, regarding silica retention are incorporated herein by cross-reference.

5 After crystallization, the microspheres contain crystalline Y-faujasite in the sodium form. In order to obtain a product having acceptable catalytic properties, it is necessary to replace sodium cations in the microspheres with more desirable cations. This may be accomplished by  
10 contacting the microspheres with solutions containing ammonium or rare earth cations or both. The ion exchange step or steps are preferably carried out so that the resulting catalyst contains less than about 0.7%, most preferably less than about 0.5% and most preferably less  
15 than about 0.4%, by weight  $\text{Na}_2\text{O}$ . After ion exchange, the microspheres are dried, preferably by flash drying, to obtain the microspheres of the present invention. In order to make 0 wt. % rare earth (REO) catalysts, the  $\text{Na}^+$  cations are exchanged by using only an ammonium salt such as  $\text{NH}_4\text{NO}_3$   
20 and without using any rare earth salt during exchange. Such 0 wt. % REO catalysts are especially beneficial as FCC catalysts that give higher octane gasoline and more olefinic product. Rare earth versions of catalysts of this invention, post treated after crystallization by ion-  
25 exchange with high levels of rare earth, e.g., by procedures such as described in the '902 patent, are useful when exceptionally high activity is sought and the octane rating of the FCC gasoline produce is not of prime importance. Rare earth levels in the range of 0.1% to 12% usually  
30 between 0.5% and 7% (weight basis) are contemplated.

The preferred catalyst of the invention comprises microspheres containing at least 50% and preferably from 70%

to 75% by weight Y-faujasite, expressed on the basis of the as-crystallized sodium faujasite form zeolite. As used herein, the term Y-faujasite shall include synthetic faujasite zeolites exhibiting, in the sodium form, an X-ray  
5 diffraction pattern of the type described in Breck, Zeolite Molecular Sieves, p. 369, Table 4.90 (1974), and having a crystalline unit cell size, in the sodium form (after washing any crystallization mother liquor from the zeolite), of less than about 24.75 Å as determined by the technique  
10 described in the ASTM standard method of testing titled "Determination of the Unit Cell Size Dimension of a Faujasite Type Zeolite" (Designation D3942-80) or by an equivalent technique. The term Y-faujasite shall encompass the zeolite in its sodium form as well as in the known  
15 modified forms, including, e.g., rare earth and ammonium exchanged forms and stabilized forms. The percentage of Y-faujasite zeolite in the microspheres of the catalyst is determined when the zeolite is in the sodium form (after it has been washed to remove any crystallization mother liquor  
20 contained within the microspheres) by the technique described in ASTM standard method of testing titled "Relative Zeolite Diffraction Intensities" (Designation D3906-80) or by an equivalent technique. It is important to equilibrate the microspheres carefully before X-ray  
25 evaluations are made since equilibration can have a significant effect on the results.

It is preferred that the Y-faujasite component of the microspheres, in their sodium form, have a crystalline unit cell size of less than about 24.73 Å and most preferably  
30 less than about 24.69 Å. Typically, the Y-faujasite component of the microspheres has a crystalline unit cell

size range of between 24.64 - 24.73 Å, corresponding to a  $\text{SiO}_2/\text{Al}_2\text{O}_3$  molar ratio of the Y-faujasite of about 4.1 - 5.2.

The microspheres of the invention may be marketed either in a pure form or blended with other catalysts, additives and/or other blending agents.

The catalysts of the present invention, like all commercial fluid catalytic cracking catalysts, will be hydrothermally deactivated during the operation of the cracking unit. Accordingly, as used herein, the phrase "cracking the petroleum feedstock in the presence of a catalyst" shall include cracking the petroleum feedstock in the presence of the catalyst in its fresh, partially deactivated, or fully deactivated form.

#### 15 Example 1

In this example a microsphere containing 60 parts of coarse white hydrous kaolin (72% < 2 µm) and 40 parts of Ansilex® 93 spinel from fractionated, pulverized, ultrafine (90% < 1 µm) gray kaolin was spray dried with 12 parts  $\text{SiO}_2$  from Grade 40 (Occidental) sodium silicate and then calcined. The microspheres were later crystallized and exchanged to form the catalyst of the invention.

The slurry for spray drying was formed by combining the hydrous kaolin stream with the spinel powder. Water was added to control the combined slurry solids to 50%. The slurry was fed to a spray dryer with a wheel atomizer, where the sodium silicate solution (2.88  $\text{SiO}_2/\text{Na}_2\text{O}$ ) was injected into the slurry at an in-line static mixer a few feet upstream of the atomizer. The mix was spray dried and then rotary calcined until the X-ray diffraction line for hydrous

kaolin was eliminated, indicating conversion of hydrous kaolin to metakaolin.

These microspheres were subsequently crystallized at about 210 deg. F. by conventional methods to yield zeolite Y. The following Table 1 lists the crystallization recipe utilized in this example.

TABLE 1

SiO <sub>2</sub> /Na <sub>2</sub> O, w/w	2.74
SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub> , w/w	6
H <sub>2</sub> O/Na <sub>2</sub> O, w/w	6.39
Seeds, w/w	0.004
Microsphere gms	250
30% Sodium Disilicate, gms	989.8
19 % NaOH, gms	17.8
H <sub>2</sub> O, gms	2.3
Hours	20

After crystallization the mother liquor was removed from the catalyst and then the catalyst was washed with water. The material was then ion exchanged with ammonium nitrate as detailed in the other examples. Rare earth was added to the catalyst. The catalyst was calcined and then further ion exchanged until a nominal 0.4 % Na<sub>2</sub>O was obtained. The catalyst was then calcined a second time to finished product. The properties of the catalyst were compared with the properties of rare earthed exchanged commercial catalysts prepared in accordance with U.S. 4,395,809. Results are shown in Table 2.

TABLE 2

Comparative Catalyst (4,395,809) Data at 1.1% REO			
	Sodium Form	Finished Product	Steamed 4 Hrs. @ 1500 F
TSA	506	373	230
MSA	56	121	81
ZSA	450	252	149
Z/M	8.04	2.08	1.84
UCS		24.48	24.26
ABD		0.86	0.86
Comparative Catalyst (4,395,809) at 3.1% REO.			
	Sodium Form	Finished Product	Steamed Properties 4 Hrs. @ 1500 F
TSA	506	407	244
MSA	56	116	77
ZSA	450	291	67
Z/M	8.04	2.51	2.17
UCS		24.52	24.292
ABD		0.83	0.85
Invention at 1.5% REO			
	Sodium Form	Finished Product	Steamed Properties 4 Hrs. @ 1500 F
TSA	564	432	272
MSA	75	132	95
ZSA	489	300	177
Z/M	6.52	2.27	1.86
UCS		24.459	24.26
ABD		0.83	0.83
Invention at 3.1% REO			
	Sodium Form	Fresh	4 Hrs. @ 1500
TSA	564	443	271
MSA	75	126	93
ZSA	489	317	178
Z/M	6.52	2.52	1.91
UCS		24.528	24.273
ABD		0.8	0.82

Example 2

- 5           The comparative and inventive (3% REO) samples of Example 1 were tested as cracking catalysts. The samples steamed at 1500 F for four hours were blended with activity-adjusting kaolin microspheres to give a BET surface area of 130 m<sup>2</sup>/gm. These blends were used in an ACE<sup>TM</sup> (Xytel)
- 10       microscale FFB reactor with a 2.125" injector, 8 WHSV, varying time on stream, 980° F, and a gas oil whose

properties are listed in Table 3. The selectivities, calculated at constant coke, are not meaningfully different between the Invention and the prior art commercial catalysts, see Table 4. The steamed surface areas and sodium  
5 removal results were improved, however.

TABLE 3

Gas Oil Properties	
Concarbon	0.36
API @ 60F	24.29
Pour Point (F)	97
Aniline Pt. (F)	189
Basic N ppm	355
Total N ppm	986
Ref. Index @25C	1.505
Sulfur%	0.72
UOP Kw	11.92
Simulated Distillation (F)	
10%	633
30%	731
50%	808
70%	887
90%	980

TABLE 4

Catalyst	Comparative	Invention
Rare Earth Content	3% REO	3% REO
H <sub>2</sub> , Wt%	0.07	0.08
Total C <sub>2</sub> -, Wt%	1.67	1.67
LPG, Wt%	19.43	19.75
Gasoline, Wt%	49.61	50.04
LCO, Wt%	15.93	16.10
HCO, Wt%	9.81	8.90
Coke, Wt%	3.54	3.54
Total	100.00	100.00
C <sub>3</sub> =/Total C <sub>3</sub> s	0.83	0.84
i-C <sub>4</sub> =/C <sub>4</sub> =	0.22	0.24
C <sub>4</sub> =/Total C <sub>4</sub> s	0.54	0.55
Conversion	74.26	75.00
Cat/Oil	6.44	7.45

Example 3.

5

In this example a microsphere containing about 67 parts of Metamax™ metakaolin and 33 parts of Ansilex® 93 spinel pigment from ultrafine (90% < 1 μm) gray kaolin was spray dried with 11.7 parts of SiO<sub>2</sub> from N-Brand® sodium silicate, acid-neutralized and then calcined. The microspheres were later crystallized and exchanged to form the catalyst of the invention.

The slurry that was spray dried was formed by mixing 2.2 kg of A-93 HS, a 60% solids aqueous slurry of Ansilex 93® high brightness pigment available from Engelhard Corporation, and 4.87 kg of Metamax™ metakaolin at about 55% solids. Metamax is available as a dry powder, also from the Engelhard Corporation. The Metamax was made down with 0.9 ml of Colloid 211 dispersant per kg of dry Metamax. The

3. The catalyst of claim 1 wherein said slurry in step (a) contains (i) metakaolin.

4. The catalyst of claim 1 wherein said microspheres of calcined kaolin in step (c) has a ratio of metakaolin to kaolin calcined through the characteristic exotherm in excess of 1.25:1.

5. The catalyst of claim 2 wherein said slurry in step (a) comprises from (i) 55 to 85 parts by weight hydrated kaolin clay and (ii) 15 to 45 parts by weight kaolin clay that has been calcined through its characteristic exotherm.

6. The catalyst of claim 3 wherein said slurry in step (a) comprises (i) 55 to 85 parts by weight metakaolin and (ii) about 15 to 45 parts by weight kaolin calcined through its characteristic exotherm.

7. The catalyst of claim 1 in which said binder is a sodium silicate solution.

8. The catalyst of claim 7 in which the binder level as  $\text{SiO}_2$  is between about 2 to 25 wt.% of the microspheres in step (b).

9. The catalyst of claim 7 in which the binder level as  $\text{SiO}_2$  is between about 4 to 17 wt.% of the microspheres in step (b).

10. The catalyst of claim 1 wherein 90 wt. % of said ultrafine kaolin is in particles having a diameter of less than 1 micron.

5 11. The catalyst of claim 1 wherein said Y-faujasite is in the sodium form.

10 12. The catalyst of claim 11 wherein at least a portion of said sodium is ion-exchanged with rare earth cations.

15 13. The catalyst of claim 1 wherein said calcined, ultrafine kaolin has an incipient slurry point of less than 57% solids.

14. The catalyst of claim 13 wherein said calcined ultrafine kaolin has an incipient slurry point of no greater than 52% solids.

20 15. A zeolitic fluid catalytic cracking catalyst produced by the steps comprising:

(a) forming a aqueous slurry containing (i) hydrated kaolin clay, metakaolin or mixtures thereof, (ii) a calcined aluminum source and (iii) binder, said calcined  
25 aluminum source having an incipient slurry point of less than 57% solids;

(b) spray drying the aqueous slurry to obtain microspheres;

(c) calcining the microspheres obtained in step  
30 (b) at a temperature and for a time sufficient to convert hydrated kaolin clay in the microspheres substantially to metakaolin, but insufficient to cause metakaolin or hydrated

kaolin to undergo the characteristic kaolin exotherm and to provide microspheres of calcined kaolin having a ratio of metakaolin to calcined aluminum source in excess of 1:1;

(d) mixing the microspheres obtained in step (c)  
5 with sodium silicate and water to obtain an alkaline slurry;

(e) heating the slurry of microspheres of calcined kaolin to a temperature and for a time sufficient to crystallize at least about 50% by weight Y-faujasite in the microspheres.

10

16. The catalyst of claim 15 wherein said slurry in step (a) comprises from (i) 55 to 85 parts by weight hydrated kaolin clay and (ii) 15 to 45 parts by weight calcined aluminum source.

15

17. The catalyst of claim 15 wherein said slurry in step (a) comprises (i) 55 to 85 parts by weight metakaolin and (ii) about 15 to 45 parts by weight calcined aluminum source.

20

18. The catalyst of claim 15 wherein said Y-faujasite is in the sodium form.

19. The catalyst of claim 18 wherein at least a  
25 portion of said sodium is ion-exchanged with rare earth cations.

20. The catalyst of claim 15 herein said calcined aluminum source has an incipient slurry point of no greater  
30 than 52% solids.

21. The catalyst of claim 1 wherein said Y faujasite is present in amount of at least 65% by weight of said microspheres.

5        22. The catalyst of claim 15 wherein said Y faujasite is present in amount of at least 65% by weight of said microspheres.

23. A method of making a high zeolite content fluid  
10 catalytic cracking catalyst comprising the steps of:  
      (a) forming an aqueous slurry containing (i) hydrated kaolin clay, metakaolin or mixtures thereof, (ii) a calcined aluminum source, (iii) sodium silicate binder, said calcined aluminum source having an incipient slurry point of  
15 less than 57% solids;  
      (b) spray drying the aqueous slurry to obtain microspheres;  
      (c) calcining the microspheres obtained in step (b) at a temperature and for a time sufficient to convert  
20 hydrated kaolin clay in the microspheres substantially to metakaolin, but insufficient to cause metakaolin or hydrated kaolin to undergo the characteristic kaolin exotherm and to provide microspheres of calcined kaolin having a ratio of metakaolin to calcined aluminum source of greater than 1:1;  
25        (d) mixing the microspheres obtained in step (c) with sodium silicate and water to obtain an alkaline slurry;  
      (e) heating the slurry of microspheres of calcined kaolin to a temperature and for a time sufficient to crystallize at least about 50% by weight Y-faujasite in  
30 the microspheres.

24. The method of claim 23 wherein at least 65% by weight Y-faujasite is crystallized in the microspheres in step (e).

5        25. The method of claim 24 wherein at least 70% by weight Y-faujasite is crystallized in the microsphere in step (e).

26. The method of claim 23 wherein said Y-faujasite is  
10    in the sodium form.

27. The method of claim 26 including the steps of:  
      (f) separating the microspheres containing at least 50% by weight Y-faujasite from at least a major  
15    portion of its mother liquor;  
      (g) replacing sodium cations in the microspheres separated in step (e) with ammonium ions or ammonium ions and thereafter rare earth ions;  
      (h) calcining the microspheres from step (g) to  
20    facilitate release of sodium ions; and  
      (i) further exchanging the microspheres with ammonium ions to reduce  $\text{Na}_2\text{O}$  content to below 1%.

28. The method of claim 27 in which the rare earth  
25    content expressed as rare earth oxide, REO, is between 0.1 wt. % and 12 wt. %.

29. The method of claim 27 in which the rare earth  
content expressed as rare earth oxide, REO, is between 0.5%  
30    wt. % and 7 wt. %.

30. The method of claim 27 in which the sodium content expressed as  $\text{Na}_2\text{O}$  is reduced to a level up to 0.35 wt. %.

31. The method of claim 23 wherein said calcined  
5 aluminum source is kaolin clay calcined through the characteristic exotherm, said kaolin clay calcined through the characteristic exotherm being derived from a pulverized ultrafine kaolin wherein 90 wt. % of said ultrafine kaolin is in particles having a diameter of less than 2 microns

10

32. The method of claim 31 wherein 90% of said ultrafine kaolin is in particles having a diameter of less than 1 micron.

15 33. The method of claim 31 wherein said kaolin calcined through said exotherm is derived from a gray clay containing at about 0.6 to 1.0 wt. % iron oxide.

34. The method of claim 23 wherein said alkaline  
20 slurry of step (d) contains sodium hydroxide.

35. The method of claim 26 comprising replacing sodium cations in the microspheres with ammonium ions and thereafter rare earth ions.

25

36. A method of cracking a gas oil comprising contacting said gas oil with a fluidized catalyst of claim 1.

30 37. A method of cracking a gas oil comprising contacting said gas oil with a fluidized catalyst of claim 15.

## INTERNATIONAL SEARCH REPORT

Int'l Application No

PCT/US 02/25023

A. CLASSIFICATION OF SUBJECT MATTER  
IPC 7 B01J29/08 B01J37/00 C10G11/05

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 B01J C10G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the International search (name of data base and, where practical, search terms used)

EPO-Internal

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P, X, L	WO 02 24329 A (ENGELHARD CORP) 28 March 2002 (2002-03-28) page 11, line 15 -page 12, line 7 page 22, line 26 -page 26, line 1 page 29, line 9 - line 12	1-37
X	US 4 493 902 A (BROWN STANLEY M ET AL) 15 January 1985 (1985-01-15) cited in the application	15-37
A	whole document, see especially Example 4	1-14
A	US 5 395 809 A (MADON ROSTAM J ET AL) 7 March 1995 (1995-03-07) cited in the application the whole document	1-37

☐ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

## \* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the International filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&amp;" document member of the same patent family

Date of the actual completion of the international search

28 November 2002

Date of mailing of the international search report

05/12/2002

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
Fax (+31-70) 340-3018

Authorized officer

Veefkind, V

Continuation of Box I.2

Present claims 15-37 relate to a compound and method defined (inter alia) by reference to the 'incipient slurry point', which apparently is derived from a test that was developed by the applicant to determine the pore volume of the calcined aluminum source.

The use of this parameter in the present context is considered to lead to a lack of clarity within the meaning of Article 6 PCT. It is impossible to compare the parameters the applicant has chosen to employ with what is set out in the prior art. The lack of clarity is such as to render a meaningful complete search impossible.

Consequently, the search has been performed for claims 15-37 as if this parameter were not present.

The applicant's attention is drawn to the fact that claims, or parts of claims, relating to inventions in respect of which no international search report has been established need not be the subject of an international preliminary examination (Rule 66.1(e) PCT). The applicant is advised that the EPO policy when acting as an International Preliminary Examining Authority is normally not to carry out a preliminary examination on matter which has not been searched. This is the case irrespective of whether or not the claims are amended following receipt of the search report or during any Chapter II procedure.

# INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US 02/25023

## Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:  
because they relate to subject matter not required to be searched by this Authority, namely:
  
2. ☒ Claims Nos.:  
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:  
see FURTHER INFORMATION sheet PCT/ISA/210
  
3. ☐ Claims Nos.:  
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

## Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this International application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.
  
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
  
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:
  
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
- ☐ No protest accompanied the payment of additional search fees.

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 02/25023

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
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